MACINNES

The Freezing Points, Conductivities, And Viscosites of Aqueous Solutions of Caesium Nitrate

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THE FREEZING POINTS, CONDUCTIVITIES, AND VISCOSITIES OF AQUEOUS SOLUTIONS OF CAESIUM NITRATE

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Duncan Mac Innes

ENTITLED The Freezing Points, Conductivities and Viscosities of Aqueous Solutions of Caesium Nitrate

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Master of Science.

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Recommendation concurred in:

Committee
on
Final Examination

THE FREEZING POINTS, CONDUCTIVITIES, AND VISCOSITIES OF AQUEOUS SOLUTIONS OF CAESIUM NITRATE.

1. General Outline of the Investigation.

It has been shown by E. W. Washburn[1] that for moderately concentrated solutions of certain non-electrolytes the relation between freezing point depression and the mol fraction of the solute follows the law developed for the "perfect solution". Deviations from this relation are to be expected where hydration, association, dissociation, etc., occur and such deviations may, in certain cases, be used to calculate, roughly at least, the extent to which these phenomena are present in a given solution. Thus, for example, the deviations observed in the case of cane sugar solutions are such as would result from the combination of six mols of water with each mol of sugar.

The purpose of the present investigation is to determine, if possible, whether the deviation from the law of the "perfect solution" in the case of a strong electrolyte can be used to calculate the degreeoof hydration of the electrolyte. To accomplish this we must have an independent means of determining the degree of ionization. If, for example, an electrolyte can be found which is not hydrated in solution and which obeys the law of the perfect solution when the degree of ionization is assumed to be that calculated from the electrical conductance, it is not unreasonable to conclude that the deviations from this law in the case of other electrolytes of the same type can be attributed

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[1] :- Technology Quarterly, Vol.XXI, No.4,1908; Jahrbuch der Radio und Elect. V.pg.493,1908.

to hydration. A number of different facts indicate that the caesium ion is the least hydrated of the ions of the alkali metals[1]. We have similar evidence indicating that the nitrate is the least hydrated of all the anions. It is not improbable, therefore, that caesium nitrate solutions might be found to show an agreement with the law of "perfect solution," and they have therefore been chosen as the subject of this investigation.

The experimental part of this investigation consists in measuring the freezing points of a series of caesium nitrate solutions ranging in concentration from .01 to.45 normal. The electrical conductance and viscosity of the same solutions at 0° have also been determined and these data are used in calculating the degree of ionization of the electrolyte.

2. Description of Apparatus and Methods.

(a) The Conductance Measurements:- A Kohlrausch slide wire bridge was used in the conductance measurements. The wire had a length of about three meters, the smallest scale division being 3 mm. It was calibrated against standard resistances by the method described by Kohlrausch and Holborn[2]. The alternating current was furnished by a small induction coil provided with an adjustable resistance in series with its primary coil for the purpose of varying the tone heard in the telephone receiver. A small adjustable condenser placed in parallel with the conductivity cell as recommended by Kohlrausch[3] greatly facilitated the determination of the null point on the wire. Using this device

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1-Washburn, Technology Quarterly,Vol.XXL No.4 ,Pg. 364.
2-Leitvermogen der Electrolyte, pg. 47.
3- " " " pg. 59.

the null point could be easily determined to .3 mm.

Conductivity cells of the pipette type represented in Fig. 1 were used in the conductance measurements. The internal diameter of the cells was 1.5 cms. and the electrodes were 7.5 and 1.5 cms. apart respectively. The electrodes were coated with platinum black in the usual manner. The conductance capacities of these cells were determined by measurements with tenth normal and normal solutions of potassium chloride made as directed by Kohlrausch and Holborn[1], the values used for the specific conductances of these solutions being those given by these authors. All conductance measurements were made at 0°, a Dewar bulb filled with chopped ice being used as a thermostat.

(b) The Specific Gravity Measurements:- The pycnometer used was of the Ostwald-Sprengel type, with a glass cap ground on the end of one capillary tube and a small bulb blown in the upper part of the other to allow for expansion of the liquid contained. This was necessary as the pycnometer was filled at 0° and weighed at room temperature. A second pycnometer was used as a counterpoise when weighing. The capacity of the pycnometers was about 25cc. All specific gravities are at 0° referred to water at 4° C.

(c) The Freezing Point Measurements:- The freezing point of an aqueous solution is the temperature at which it is in equilibrium with ice. To obtain this temperature accurately it is necessary to have the two phases in intimate contact. The Beckman method is not suited for accurate work as one can never be certain that equilibrium has been reached owing to the small amount of ice separating out. Corrections must also be applied

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[1] Leit. der Elect. pg. 76.

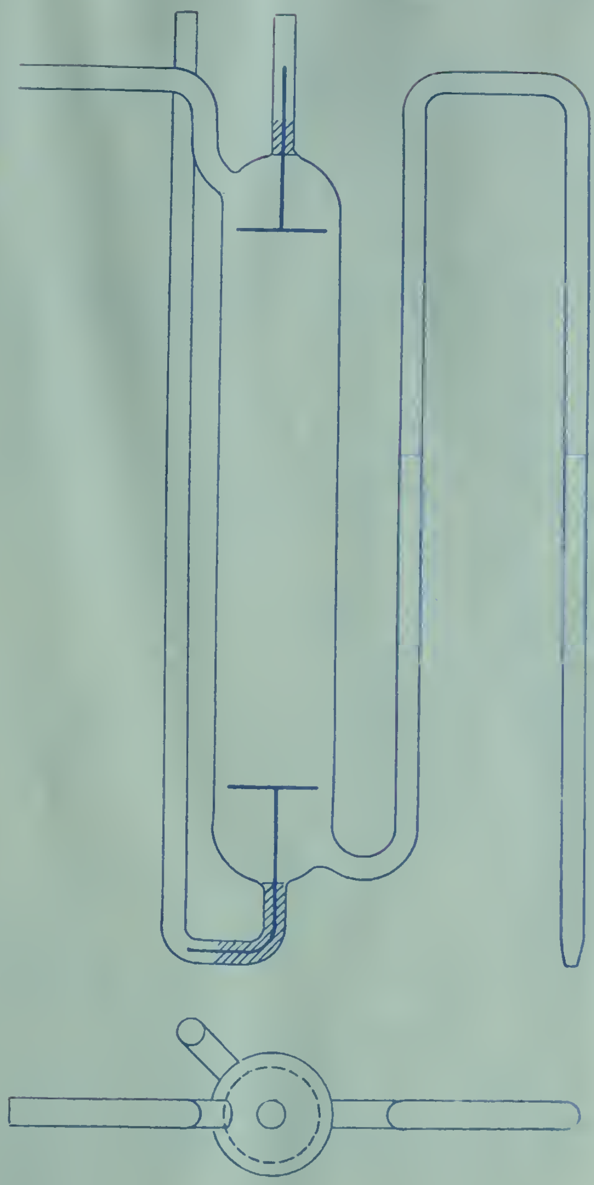

Fig 1.

for the "convergence temperature", for concentration changes due to the separation of ice, etc. It was therefore decided to use the following method which has been fully described by T. W. Richards[1].

Pure ice was prepared by placing test tubes containing conductivity water in a freezing mixture. The ice collected on the walls of the test tubes and the central portions, containing any impurities present, was poured off. The ice was then broken into small lumps in a mortar that had been previously chilled by filling it with fine ice. The lumps were next transferred to a cylindrical Dewar bulb until the inner tube was about three fourths filled. The caesium nitrate solution whose freezing point was to be determined was cooled by a freezing mixture and then poured over the ice in the Dewar bulb. A Beckman thermometer and a stirrer were then inserted and the vessel covered. The mixture of ice and solution was then slowly stirred until the thermometer gave constant readings. During this time the thermometer was tapped regularly by an electrical device. As quickly as possible after reading the thermometer a portion of the solution from the region near the thermometer bulb was drawn off into the conductivity cell, the pyknometer being filled immediately afterwards in a similar manner. The conductivity cell was then placed in an ice bath in a Dewar bulb. The bath was stirred constantly, and as soon as the contents of the cell had assumed the temperature of the bath the conductance was measured. A Portion of the solution from the conductivity cell was used later for the viscosity measurements.

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[1] Jour. Am. Chem. Soc., pg. 291, Vol. 25, 1903.

A diagram of the apparatus is shown in Fig. 2. The Dewar bulb had a capacity of 180 cc. and was silvered to diminish radiation. A wire stirrer and the Beckman thermometer passed through holes in the cover. "A" is an electrically operated tapper.

The Beckmann thermometer was carefully calibrated for irregularities of bore by the usual method of a moving mercury thread. The value of the degree in terms of the hydrogen gas thermometer was found by comparison with two thermometers standardized by the Bureau of Standards. Readings of the thermometer were always made with the meniscus of the mercury slowly rising. Two weeks before beginning the freezing point measurements the Beckmann thermometer was placed in an ice bath and when not in use it was kept in the ice bath throughout the investigation.

(d) The Viscosity Measurements:- The viscosimeters used were of the Ostwald type, having a time of flow for water at 0° of about 200 seconds. All measurements were made at 0o in an ice bath contained in a Dewar bulb with unsilvered walls. As the incoming air showed a tendency to warm the bulb above the capillary tube and thus give too low values for the viscosity, the solution was drawn into the bulb and the other tube of the viscosimeter was stoppered to prevent the solutions running down until the whole had reached the temperature of the bath. The stopper was then withdrawn and the time of flow taken as usual with a stop watch.

The weights used in this investigation were calibrated by the method described by T. W. Richards[1] and all weighings have been reduced to vacuo.

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[1] Jour. of Am. Chem. Soc. 22, pg. 144, 1900.

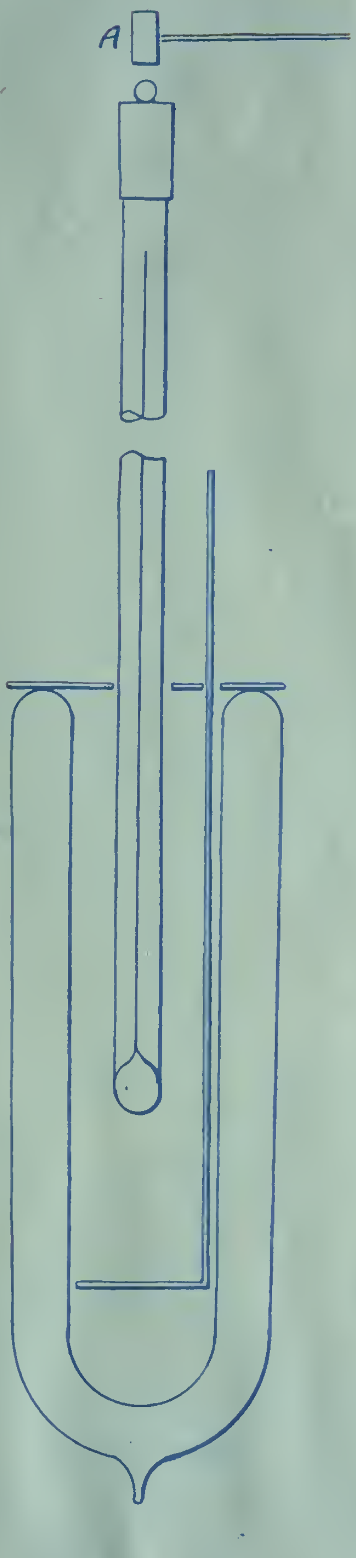

Fig. 5

3. Purification of Materials.

Caesium Nitrate:- The method of purification used was that described by J. Lawrence Smith[1]. Kahlbaums purest caesium carbonate was dissolved in the smallest amount of nitric acid. Solid iodine and hydrochloric acid were added in the proportions necessary to form $Cs\ Cl_2\ I$, and the mixture was heated. The caesium chlor-iodide separated as orange colored crystals upon cooling. The crystals were filtered from the mother liquor and dried as far as possible by suction. The crystallization was repeated three times from hot hydrochloric acid (1 to 1), drying the crystals between each two operations. The final product was heated slowly over a flame in a casserole to remove the iodine and the excess chlorine and the resulting caesium chloride was converted into nitrate by four evaporations with pure nitric acid. (The pure nitric acid was obtained by distilling ordinary pure acid and reserving the second third of the distillate.) The caesium nitrate thus obtained was crystallized four times from conductivity water and the final product was dried in an air bath.

Potassium Chloride:- Kahlbaum's purest potassium chloride was recrystallized four times from conductivity water and dried between filter paper. For the preparation of the stock solutions the purified salt was fused and weighed in a platinum crucible.

Water:- All the water used in this investigation was conductivity water obtained from the special still in this laboratory. It had a specific conductivity at 0° of 1.2×10^{-6} mhos.

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[1] Amer. Jour. of Sci.,II. 16, pg. 373.

4. Preparation and Analysis of Solutions.

As there is no quick and accurate method for determining caesium, it was decided to determine the concentration of the solutions whose freezing points had been measured by determining the specific conductance of the solutions. Accordingly a stock solution was prepared and carefully analysed by the method given below and a series of solutions of known concentration was prepared from this by diluting with conductivity water. The specific conductance of each solution was measured and the results were plotted using concentration and specific conductance as coordinates. From this curve the concentration of any solution within the limits covered by the experiments could be found when its specific conductance was known. The stock solution of caesium nitrate was kept well stoppered in a Jena glass flask that had been steamed to remove all soluble constituents from its inner surface. The series of solutions of known concentration was made by drawing off portions of this solution with a pipette and transferring to small glass stoppered Erlenmeyer flasks of Jena glass, the weights of which were known. After weighing carefully, conductivity water was added in the required amount and the solution again weighed. Unnecessary exposure to the air was avoided in order to minimise the error due to evaporation.

The caesium nitrate content of the stock solution was found by weighing out a portion of about forty grams into a small Jena glass flask. This flask was then placed in a paraffin bath which was kept at a temperature between 96 and 98° C. A slow current of filtered air was passed into the neck of the flask during the evaporation. After evaporation to dryness and cooling, 25 cc. of pure hydrochloric acid was added and the evapor-

ation to dryness was carried out as before; this was repeated three times. The caesium chloride thus obtained was then heated in an air bath to constant weight. The temperature of the air bath was kept between 200° and 225° as it was found that on prolonged heating above the latter temperature there was a slight loss due to volatilization of caesium chloride. An empty flask was used as a counterpoise and was put through the same series of operations to guard against any error due to change of weight of the flask. It was found possible to obtain an accuracy of about .03% by this method, as the following results for the concentration of the stock solution show:-

	Weight of solution used for analysis	Weight of Cs Cl obtained	Percent of $CsNO_3$
1	44.4471	3.7764	9.795
2	34.5616	2.8780	9.796
3	34.0061	2.8688	9.798

5- Results

The results of the specific conductance measurements at 0° together with the corresponding concentrations of the series of solutions prepared by diluting the stock solution are given in columns 1 and 3 of table 1. The curve representing these results is shown in Fig. 3, curve A, using concentrations as abscissae and specific conductances as ordinates. The densities of this series of solutions are given in column 5, table 1. Column 4 contains the equivalent conductances (Λ) which are plotted against the concentrations in mols per kilogram of water in curve

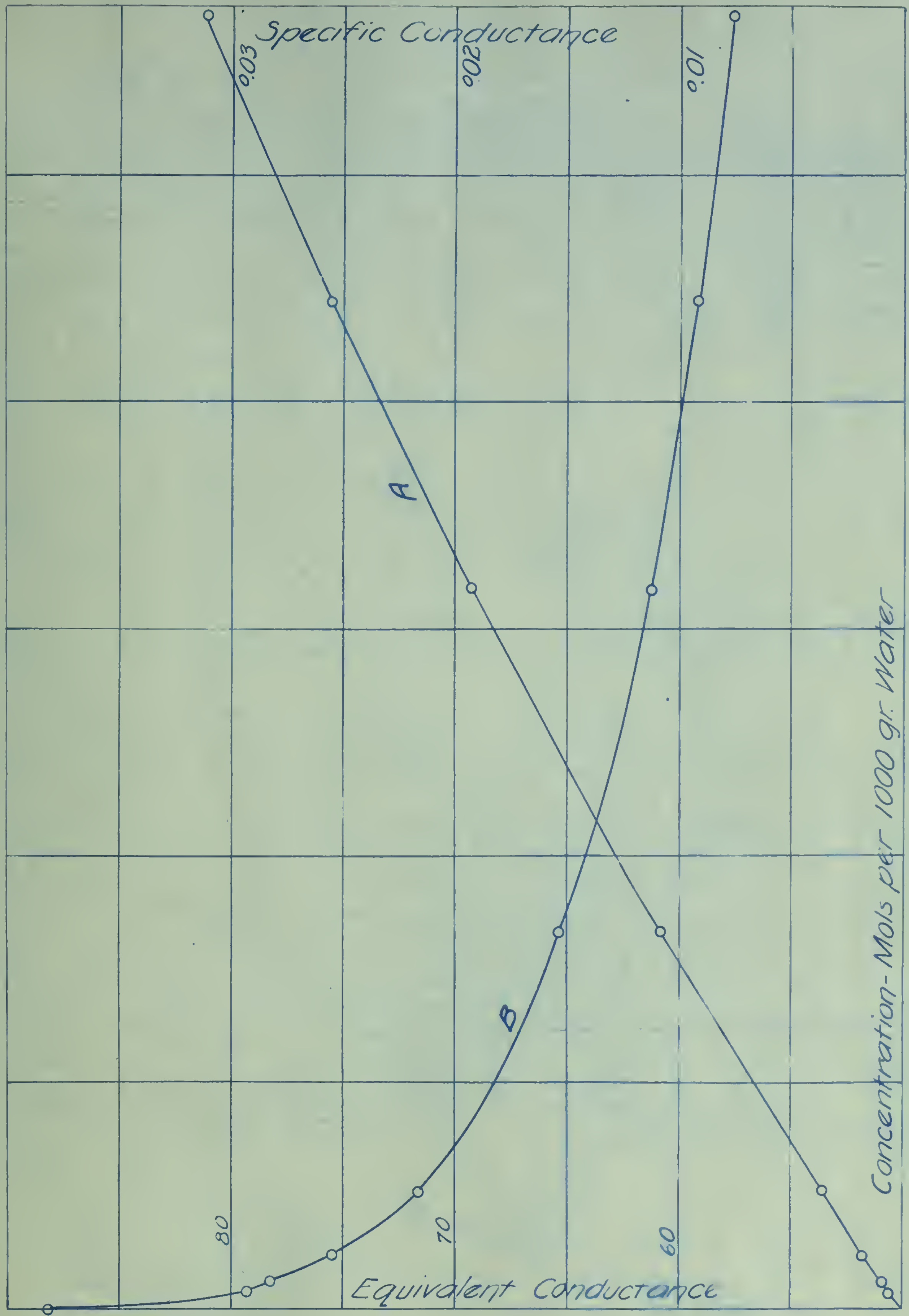
Specific Conductance
0.03
0.02
0.01
A
B
Equivalent Conductance
80
70
60
Concentration-Mols per 1000 gr. Water
0.1
0.2
0.3
0.4
0.5

Fig 3

B, Fig.3. The value of the equivalent conductance at infinite dilution was found by extrapolation, using a method proposed by A. A. Noyes[1]. This method consists in plotting values of the equivalent resistance $(\frac{1}{\Lambda})$ against the corresponding values of $(C\Lambda)^n$ where "C" represents the concentration in mols per liter and "n" is a constant for which successive values were assumed until the curve obtained became a straight line. In the present case the best value for this constant was found to be .40. The value of the intercept where "C" equals zero gives the equivalent resistance at infinite dilution. This curve is shown in Fig. 4 with values of the equivalent resistance as ordinates, and the corresponding values of $(C\Lambda)^n$ as abcissae.

Table 1.

1 No.	2 Concentration-Mols per Kg.H_2O	3 Concentration-Mols per liter	4 Sp.Cond.	5 Eq.Cond.	Sp.Gravity.
Orig.	.5572	.5432	.03125	57.51	1.0809
1	.4447	.4354	.02574	59.106	1.0638
2	.3183	.3136	.01919	61.20	1.0462
3	.1667	.1656	.01081	65.279	1.0259
4	.05081	.05086	.003636	71.528	1.0110
5	.02439	.02442	.001844	75.51	1.0062
6	.01234	.01237	$.0_39683$	78.278	1.0048
7	.008096	.008096	$.0_36417$	79.338	1.0038
	0	0		88.104	

In table 2, column 1, are given the values of the specific conductances of the solutions whose freezing points are given in

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[1] Carnegie Institute, Washington, Publication No. 63, pg.50

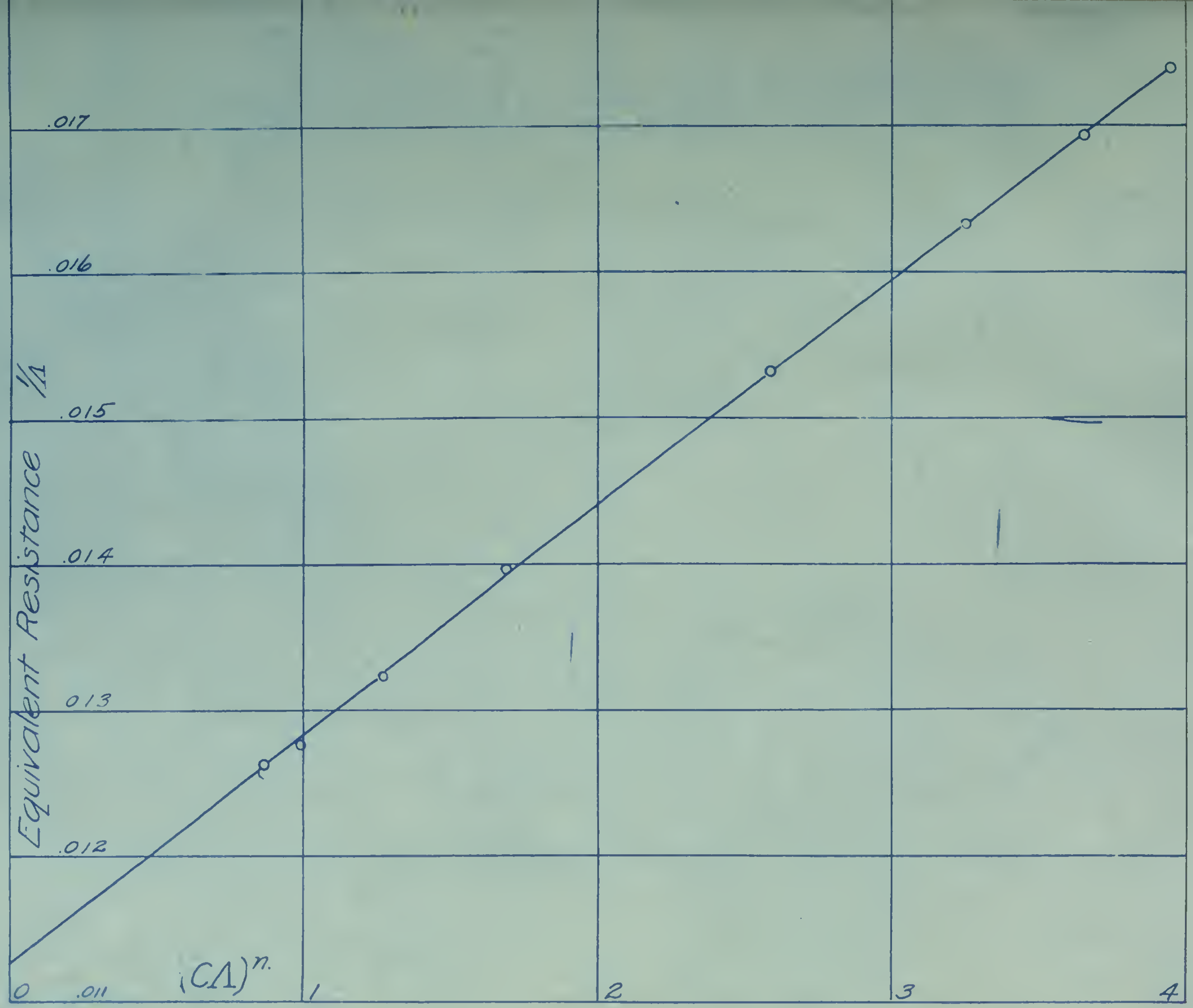
Equivalent Resistance
1/Λ
.017
.016
.015
.014
.013
.012
0
.011
(CΛ)^n.
1
2
3
4

Fig. 4.

column 3. The concentrations of these solutions were determined from the specific conductances as described in the previous section, using a specific-conductance-concentration curve drawn on a scale large enough to include all the accuracy of the measurements. The values thus determined are given in column 2 of table 2. A few values of the relative viscosities of the stronger solutions are shown under column 4. Curve "A" of Fig. 5 is drawn using concentrations as abscissae and freezing point lowerings as ordinates.

Table 2.

	1	2	3	4
Solution.	Sp. Cond.	Concentration.	Freezing Pt.	Viscosity.
1	.026105	.4521	-1.268	.921
2	.02492	.4285	-1.217	.948
3	.01670	.2708	-.822	
4	.01507	.2402	-.721	
5	.01350	.2125	-.656	
6	.01152	.1784	-.537	
7	.009165	.1381	-.434	
8	.007398	.1090	-.361	
9	.005367	.0766	-.262	
10	.003855	.0537	-.170	
11	.001771	.02315	-.093	
12	.001475	.0189	-.068	

Solution No.1 was in equillibrium with both the solid caesium nitrate and ice and the corresponding temperature is therefore the cryohydric point. This point was determined carefully using two different samples.

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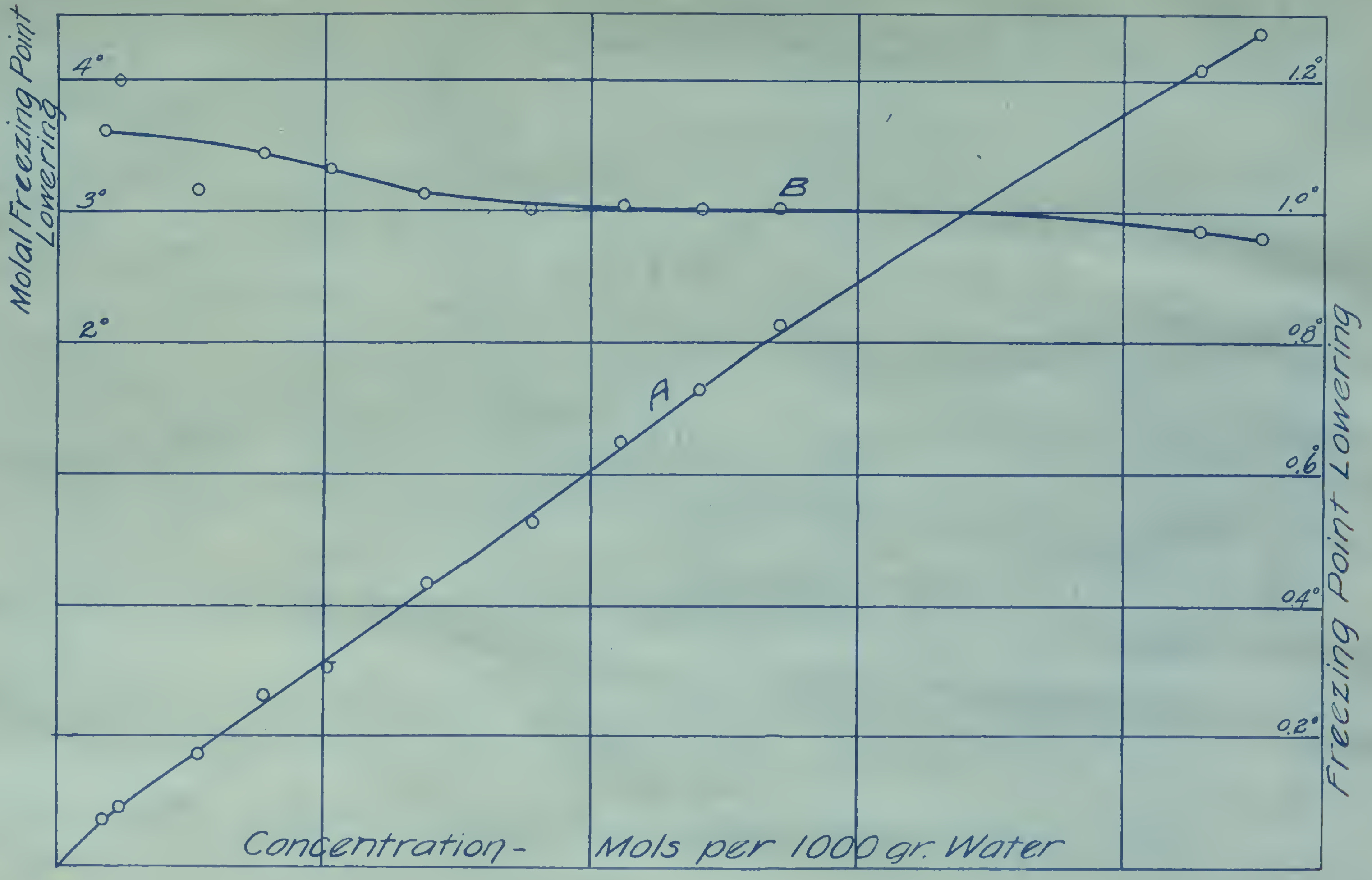

Molal Freezing Point Lowering
4°
3°
2°
B
A
1.2°
1.0°
0.8°
0.6°
0.4°
0.2°
Freezing Point Lowering
Concentration - Mols per 1000 gr. Water

Fig 5.

6- Discussion of Results.

In the case of an electrolyte that is hydrated in solution a pronounced minimum is observed in the curve showing the relation between the "molecular freezing point lowering" and the concentration[1]. This minimum occurs between the concentrations of .1 to .4 molal, and the curve rises rapidly after this point. This curve for caesium nitrate is shown in Fig. 5, curve "B", in which concentrations are plotted as abscissae and "molal freezing point lowerings" as ordinates. The absence of any minimum is evident. The curve falls regularly as would be expected for an ionized solute, which remains unhydrated.

For aqueous solutions which obey the law of the "perfect solution" the following relation between the mol fraction (N') of the solute and the freezing point lowering (Δt) has been derived thermodynamically by E. W. Washburn[2]:-

$$N = 0.0096895(\Delta t - 0.00425\,\Delta t^2) \qquad (1)$$

For a solution containing n mols of a nonelectrolyte in 1000 grams of water the mol fraction of the solute is expressed by the equation:-

$$N' = \frac{n}{\frac{1000}{18} + n} \qquad (2)$$

For an electrolyte that dissociates into two ions this relation obviously becomes:-

$$N = \frac{n(1+\alpha)}{\frac{1000}{18} + n(1+\alpha)} \qquad (3)$$

where α is the degree of ionization of the solute.

The degree of ionization of an electrolyte is usually calculated from the ratio of the equivalent conductances, the formula being:-

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[1] See Jones and Bassett, Am.Chem.Jour., 33, 534, (1905)
[2] Technology Quarterly, Vol. XXI, No.4, (1908).

$$\alpha' = \frac{\Lambda_n}{\Lambda_\infty} \qquad (4)$$

where Λ_n represents the equivalent conductance at the corresponding concentration and Λ_∞ is the equivalent conductance at infinite dilution. Values of Λ_n are given under column 1 of table 3, and the corresponding values of the degree of ionization are given in column 2 of the same table. This calculation is based on the assumption that the mobility of an ion is independent of the concentration of the solution, an assumption which is obviously incorrect, as, for moderate concentrations, the nature of the medium through which the ion is moving is quite different from the pure solvent as is shown by the change of its viscosity with increasing concentration.

The mobility of an ion is a function of the fluidity of the medium through which it moving. If we knew the form of this function for each ion we could calculate the degree of ionization for moderately concentrated solutions. It has been suggested by several investigators that the mobility is inversely proportional to the first power of the viscosity of the solution. If this is correct the degree of ionization of a solution would be given by:-

$$\alpha'' = \frac{\Lambda_n}{\Lambda_\infty}\eta_n \qquad (5)$$

where η_n is the viscosity of the solution referred to that of water as one. Values of the degree of ionization calculated from formula 5 are given in column 4 of table 3, and the viscosities used are to be found in column 4 of table 2.

The mol fraction of the solute as calculated from equation

3, using the value of the degree of ionization determined from equation 4, are given under column 3 of table 3. The corresponding mol fractions using the degree of ionization as corrected for the viscosity of the solution(formula 5) are to be found under column 5 of the same table.

Table 3.

	1	2	3	4	5
	Λ	α'	N'	α''	N''
1	58.90	.6685	.01364	.6157	.01298
2	59.25	.6725	.01273	.6375	.01247
3	62.30	.7071	.008252		
4	63.20	.7173	.007370		
5	63.80	.7241	.006551		
6	64.90	.7366	.005546		
7	66.40	.7537	.004340		
8	67.80	.7695	.003460		
9	69.60	.7900	.002462		
10	71.25	.8087	.001747		
11	75.75	.8597	$.0_37743$		
12	76.50	.8683	$.0_36351$		

The graph of the theoretical freezing point equation (Equation 1) is shown in figure 6 in which the abscissae represent mol per cent (100N). The freezing point data obtained with caesium nitrate have been plotted against corresponding values of mol per cent on this same sheet. The circles represent points for which N was calculated by means of equation 4 and the squares represent points for which N was calculated by means of equation

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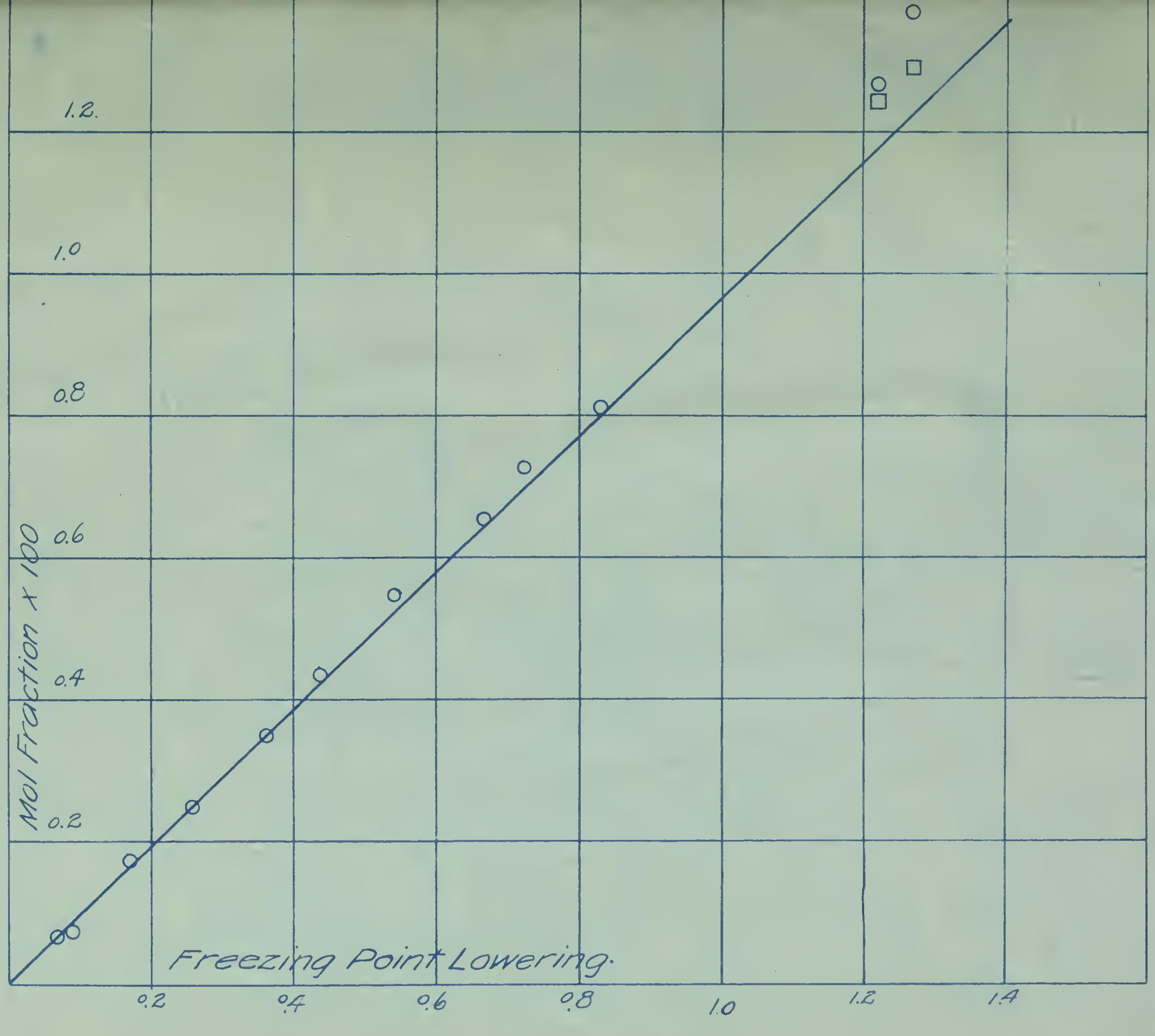
Mol Fraction x 100
1.2.
1.0
0.8
0.6
0.4
0.2
Freezing Point Lowering.
0.2
0.4
0.6
0.8
1.0
1.2
1.4

Fig 6

5. Union between solvent and solute would cause the points to fall below the graph for the freezing point equation. It is there-fore evident that the freezing point data do not indicate any hydration in solution, the deviations, in fact, being in the opposite direction. No special significance can be attached to these deviations in the case of caesium nitrate because they are such as would be expected if the mobility of the ions were proportional to some power of the viscosity higher than the first.

The investigation will be extended to solutions of lithium chloride, which is a salt of the same type as caesium nitrate but which exhibits a high degree of hydration in solution. It is hoped that from a comparison of the data from these salts it will be possible to draw some conclusion with regard to the amount of water combined with lithium chloride. It is significant that for all the caesium nitrate solutions investigated in which the viscosity differed by not more than .1% from that of pure water (i.e. up to a concentration of .27 mol per 1000 grams of water) the solution behaves as a "perfect solution."